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(19)

(54) NEW WEED-KILLERS FOR THE DESTRUCTION OF WEEDS GROWING IN VARIOUS TYPES OF GROUND

(71) We, SOCIETE NATIONALE DES PETROLES D'AQUITAINE, a French body corporate, of Tour Aquitaine, 92 Courbevoie, France, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention concerns new weed-killers which can be used, notably by leaf spraying, to destroy any spontaneous flora existing in food crops, particularly in vine-growing or tree-growing areas, and can also be used as a total weed-killer to clear courtyards and paths, without any serious risk for nearby crops or plants.

More specifically, the present invention concerns weed-killer combinations obtained from two individual weed-killers in which an unexpected synergic effect causes a degree of activity that overcomes the inadequacies involved in each of the separate weed-killers used in these combinations.

A wide variety of weeds develops in fruit crops in particular. A list of the weeds met with in argillaceo-calcareous and silicio-argillaceo-calcareous ground is given below. This list, which is given for guidance and is not exhaustive, gives the varieties of plants observed in decreasing order of frequency per square metre. In silicio-argillaceo-calcareous ground, the varieties observed include common groundsel, scarlet pimpernel, chickweed, creeping buttercup, purslane, meadow speedwell, corn sow-thistle, rumex (sorrel), greater plantain, spear-shaped plantain, goosegrass, toad-flax, bear's-bind, thistle, goosefoot, ray-grass, meadow-grass, shiny crane's-bill, dandelion, couchgrass, wart-wort, knotgrass, mallow, white clover, and black nightshade. In argillaceo-calcareous ground, the varieties observed include scarlet pimpernel, bear's-bind, ray-grass, meadow speedwell, shiny crane's-bill, spear-shaped plantain, greater plantain, succory, white clover, goosegrass and madder-wort.

Many weed-killers already exist for the destruction of these weeds, notably two commercial weed-killers known as "Paraquat", an aqueous solution of 200 g/l of 1.1'-dimethyl, 4.4'-dipyridilium dichloride with a density of 1.1 at 20°C, and "Dichlobenil", a powder for wetting containing 50% weight of 2.6-dichloro-benzonitrile. Each of these weed-killers is effective with a number of plants, using the doses recommended by the manufacturers. However, the effect drops sharply, or disappears entirely, when the concentration used is considerably reduced. In addition, these weed-killers have no effect on certain highly resistance plants such as toad-flax, bear's-bind, sorrel, mallow, and so on.

The applicant has shown that careful mixtures of these two weed-killers made them effective, through an unexpected synergic effect, against plants that were normally not destroyed by either of the weed-killers separately and that the synergic effect could be strengthened by the presence in the mixtures of dimethylsulphoxide, enabling the synergic weed-killer compositions to be used in low-concentration solutions or suspensions, with the resulting reduction in the risks of poisoning land, and significant savings in weed-killer consumption.

The most effective compositions according to the invention allow fast and almost total destruction of weeds growing in argillaceo-calcareous or silicio-argillaceo-calcareous ground.

Weed-killers, according to the invention, are characterized by the fact that they contain, as herbicidal substances, 1.1' - dimethyl, 4.4' - dipyridilium dichloride, combined with 2.6 - dichloro - benzonitrile.

Recommended weed-killers according to the invention also include dimethylsulphoxide as a third essential ingredient to reinforce the effect of the two herbicidal ingredients.

The ratio of the weight 2.6 - dichloro - benzonitrile to the weight of 1.1'-dimethyl, 4.4'-dipyridilium dichloride in weed-killers ac-

cording to the invention may be of any value, but it is preferably between 2:1 and 20:1.

In recommended weed-killers, containing, as essential ingredients, 1.1'-dimethyl, 4.4'-dipyridilium dichloride, 2.6 - dichloro - benzonitrile and dimethylsulphoxide, the overall proportion of 1.1'-dimethyl, 4.4'-dipyridilium dichloride and 2.6 - dichloro - benzonitrile may vary from 0.5 to 25%, and preferably 2 to 15%, of the total weight of the three compounds.

When the destruction of plants which have leaves with a thick, waxy limb, such as thistles, mustard, madder-wort, presents difficulty, it is recommended to acidify the weed-killers according to the present invention. For this purpose, any mono- or polyfunctional inorganic or organic acid may be used, provided that it does not cause any physical or chemical change in the compositions, and does not reduce their herbicidal effect. For instance, oxalic acid, hydrochloric or citric acid may be used, without the invention being confined to these.

Weed-killers according to the invention may also contain certain additives such as surface-active agents, provided that these additives do not have any effect on the active substances in the weed-killers.

Weed-killers according to the invention are generally prepared in the form of concentrated pastes or aqueous suspensions, which are diluted to the required concentration with water, just before use.

For this preparation, the various ingredients used in the formula of the weed-killer, taken in chemically pure form or in the form of commercial products, are mixed in suitable proportions by any method ensuring that the mixtures obtained will be as homogeneous as possible.

As an example, instructions are given below for the preparation of weed-killers in the form of aqueous concentrates from dimethylsulphoxide and the commercial weed-killers "Paraquat" and "Dichlobenil" as defined above.

The selected proportion of "Paraquat" is added gradually to the required quantity of "Dichlobenil", while the mixture is stirred to avoid lumps forming. The dimethylsulphoxide is then added in a suitable proportion, the mixture being stirred to ensure proper homogenization.

The diluted weed-killers can also be prepared directly just before application, by mixing the ingredients at the required concentrations.

The total proportion of herbicidal substances, namely 1.1'-dimethyl, 4.4'-dipyridilium dichloride and 2.6-dichloro-benzonitrile, in the diluted solution for application depends mainly on the degree of hardness of the weeds to be destroyed and their stage of development. The proportion is preferably between 0.05 and 1.5% of the weight of the aqueous solution.

The mixture may be applied to weeds by any suitable means, such as using a conical mist-jet spray providing fine drops. The volume of selection applied per unit of area will depend on the flow selected.

The present invention is illustrated by, while not being confined to, the following examples. Example I is a comparative example and is outside the scope of the invention.

In these examples, the tests are carried out on a vineyard planted with Ugni-Blanc vines on Telekki 5 BB stocks in silicio-argillaceo-calcareous ground, and on 41 B stocks in argillaceo-calcareous ground.

Each plot treated covers an area of 60 square metres, represented by an area of ground between two rows of vines, measuring 2 metres by 30 metres. An untreated plot was left on each side of the test plot, as a control, to check the weeds to be destroyed.

The weed-killer solutions used were applied at the rate of 1,000 litres per hectare.

Observations of the destruction of weeds were carried out regularly, and a mark from 0 to 10 was given after each observation, depending on the intensity of burning, according to the following scale:

0 : plants unharmed
1 : a few leaves beginning to dry up
2 : a few burns, in the form of spots
3 : more pronounced drying
4 : widespread burning of the leaves at the tip
5 : bands of serious burning of the limb of the leaves, covering half the leaf-surface, and numerous leaves withered
6 : tip dead; very extensive withering
7 : burning of 70% of the leaf-surface
8 : plants completely withered
9 : plants practically dry
10 : plants totally burned.

Example I.

Weed-removal tests on silicio-argillaceo-calcareous ground were carried out on 8 October 1969, using as weed-killer solutions first an aqueous solution of 1,500 g/hl of "Dichlobenil" with 50% 2.6-dichloro-benzonitrile (Test A) and second an aqueous solution of 550 g/hl "Paraquat" with 200 g/l of 1.1'-dimethyl, 4.4'-dipyridilium dichloride (test B). These doses were those normally used for each of these weed-killers.

Each solution was spread onto the corresponding plot.

The results of these tests are shown in Table I, where the numbers corresponding to the degree of destruction observed on the dates of observation indicated, are to be found opposite each variety of weed.

Examination of the results of Table I show that each of the weed-killers causing serious burning of a large number of weeds. However, the 2.6-dichlorobenzonitrile has no effect on toad-flax, bear's-bind, mallow and white clover, and only a temporary effect and to a varying degree on couchgrass, shiny crane's-bill, dandelion, sorrel and meadow speedwell.

TABLE I

Type of Weed	Test A				Test B				
	20/10 1969 (*)	27/10 1969	8/11 1969	14/1 1970	8/10 1969 (**)	9/10 1969	10/10 1969	14/10 1969	8/11 1969
Thistle	0	5	7	9	0	5	9	9	9
Goosefoot	0	5	7	9	2	5	9	9	9
Couchgrass	0	5	7	0 (a)	2	5	9	9	9
Wart-wort	3	5	7	9	0	5	9	9	9
Shiny crane's-bill	3	5	7	0 (a)	0	5	9	9	9
Greater plantain	2	5	7	9	2	5	9	9	0 (a)
Goosegrass	0	5	7	9	0	5	9	9	9
Corn sowthistle	0	5	7	9	0	5	9	9	9
Toad-flax	0	0	0	0	0	0	0	0	0
Bear's-bind	0	0	0	0	0	0	0	0	0
Mallow	0	0	0	0	0	0	2	2	2
Black nightshade	0	5	7	9	0	5	9	9	9
Scarlet pimpernel	0	5	7	9	0	5	9	9	9
Chickweed	3	5	7	9	0	5	9	9	9
Meadow-grass	0	5	7	9	0	5	9	9	9
Dandelion	2	5	2	0 (a)	2	5	9	9	0 (a)
Spear-shaped plantain	2	5	7	9	2	5	9	9	0 (a)
Purslane	0	5	7	9	0	5	9	9	9
Ray-grass	0	5	7	9	0	5	9	9	9
Creeping buttercup	0	5	7	9	0	5	9	9	9
Knotgrass	0	5	7	9	0	5	9	9	9

TABLE I (Continued)

Type of Weed	Test A				Test B				
	20/10 1969 (*)	27/10 1969	8/11 1969	14/1 1970	8/10 1969 (**)	9/10 1969	10/10 1969	14/10 1969	8/11 1969
Rumex (sorrel)	0	0	2	0 (a)	2	5	9	2 (a)	0 (a)
Common groundsel	3	5	7	9	2	5	9	9	0 (a)
White clover	0	0	0	0	0	5	7	2 (a)	0 (a)
Meadowspeedwell	0	5	7	0 (a)	0	5	9	9	0 (a)

(*) The first effects appeared 12 days after treatment.

(**) The first effects occurred 6 hours after application.

(a) Growth restarts.

The 1.1'-dimethyl, 4.4'-dipyridilium dichloride was ineffective against toad-flax and bear's-bind. Its effect was slight on mallow, and temporary on plantains, dandelion, sorrel, groundsel, white clover and meadow speedwell.

Example 2.

This example illustrates the synergic effect resulting from the combination of 2.6-dichlorobenzonitrile and 1.1'-dimethyl, 4.4'-dipyridilium dichloride.

The test was done on 8 October 1969, on weeds in a plot of silicio-argillaceo-calcareous ground, using an aqueous suspension containing 1,500 g/hl of "Dichlobenil" with 50% 2.6-dichloro-benzonitrile and 550 g/hl of "Paraquat" with 200 g/l of 1.1' dimethyl, 4.4' dipyridilium dichloride.

This mixture was spread on the leaves of the weeds. The results of the test are shown in Table II.

Comparison of the results of Table II with those of Table I show that the combination of 2.6-dichloro-benzonitrile and 1.1'-dimethyl, 4.4'-dipyridilium dichloride results, through an unexpected synergic effect, in a major phytotoxic effect on plants on which neither of these ingredients have a herbicidal effect, such as toad-flax and bear's-bind, or only a slight or temporary effect, such as white clover, meadow speedwell and sorrel. In addition, the mixtures thus obtained act faster than the separate ingredients, and their effect is long-lasting.

TABLE II

Type of Weed	Notes corresponding to the destruction observed on the dates below			
	8.10.69	9.10.69	10.10.69	8.11.69
Thistle	5	9	9	9
Goosefoot	4	8	9	9
Couchgrass	5	7	9	9
Wart-wort	4	9	9	9
Shiny crane's bill	3	7	9	9
Greater plantain	3	6	9	9
Goosegrass	4	8	9	9
Corn sowthistle	2	6	9	9
Toad-flax	2	5	7	8
Bear's bind	2	4	6	7
Mallow	2	5	7	8
Black nightshade	3	6	9	9
Scarlet pimpernel	4	7	9	9
Chickweed	5	8	9	10
Meadow grass	3	7	9	9
Dandelion	4	8	9	9
Spear-shaped plantain	3	6	9	9
Purslane	2	7	9	9
Ray-grass	3	8	9	9
Creeping buttercup	4	7	9	9
Knotgrass	3	7	9	9
Rumex (sorrel)	4	7	9	9
Common groundsel	3	7	9	9
White clover	2	6	7	7
Meadow speedwell	3	7	9	9

Example 3.

This example shows the activation by dimethylsulphoxide of the herbicidal power of "Dichlobenil" and "Paraquat", mixed together and used at concentrations ten times weaker than their normal doses.

The solutions H_1 and H_2, the compositions of which is shown in Table III, were prepared.

TABLE III

	Test H_1	Test H_2
	Concentration per hl	Concentration per hl
Dichlobenil	150 g	150 g
Paraquat	50 g	50 g
Dimethylsulphoxide		1,800
Water	Dilution to 100 l	Dilution to 100 l

Solution H_1 was prepared directly by mixing the ingredients.

Solution H_2 was obtained by preparing a 2% dilute of the concentrated composition, containing 7.5% weight of 50% "Dichlobenil", 2.5% weight of 200 g/l "Paraquat", and 90% weight of dimethylsulphoxide.

The aqueous solutions obtained were spread onto the weeds growing silicio-argillaceo-calcareous ground on 8 October 1969.

TABLE IV

Type of Weed	Test H_1				Test H_2			
	9/10 1969	10/10 1969	14/10 1969	8/11 1969	9/10 1969	10/10 1969	14/10 1969	8/11 1969
Thistle	2	5	5	5	4	5	5	5
Goosefoot	0	0	0	0	0	5	5	5
Couchgrass	0	0	0	0	0	5	5	5
Wart-wort	0	0	0	0	0	5	5	5
Shiny crane's-bill	0	0	0	3	0	5	5	5
Greater plantain	0	0	0	0	0	5	5	5
Goosegrass	0	0	0	0	0	5	5	5
Corn sow-thistle	0	0	0	0	0	5	5	5
Toad-flax	0	0	3	3	0	5	5	5
Bear's-bind	0	0	3	3	1	3	3	3
Mallow	0	0	0	0	0	5	5	5
Black nightshade	0	0	0	0	0	5	5	5
Scarlet pimpernel	1	8	8	8	0	5	5	5
Chickweed	1	8	8	8	0	5	5	5
Meadow-grass	0	0	0	0	0	5	5	5
Dandelion	0	0	0	0	8	8	8	8
Spear-shaped plantain	0	0	0	0	0	5	5	5
Purslane	0	0	0	0	0	5	5	5
Ray-grass	0	0	0	3	0	5	5	5
Creeping buttercup	0	0	0	0	0	5	5	5
Knotgrass	0	0	0	0	0	5	5	5
Rumex (sorrel)	3	7	7	7	8	8	8	8
Common groundsel	1	6	6	8	8	8	8	8
White clover	1	1	1	1	0	5	5	5
Meadow speedwell	0	0	0	0	0	2	2	2

The results of the treatments are shown in Table IV, where the numbers corresponding to the destruction observed on the date shown are given opposite each type of weed.

The herbicidal effect of H_1 is generally lower than that of formulae A and B in example 1, which seems normal in view of the concentration of active ingredients in H_1, which is ten times lower. However, the synergic effect resulting from the combination of 2.6-dichlorbenzonitrile ("Dichlobenil") and 1.1'-dimethyl, 4.4'-dipyridilium dichloride ("Paraquat"), illustrated for the high concentrations of active ingredients in example 2, already occurs for low concentrations, for a few weeds which are difficult to destroy.

The effect on toad-flax and sorrel is increased by dimethylsulphoxide. The dimethylsulphoxide itself has a synergic effect on the mixture of the two weed-killers in attacking mallow, dandelion and white clover, as is shown by the results of Test H_2 compared with those for tests A, B and H_1.

Example 4.

This example shows the favourable effect of acidifying the weed-killer mixture.

The test solution was applied on 8 October 1969 to weeds on silicio-argillaceo-calcareous ground. It was prepared by diluting in water 2% of a concentrated mixture H_3, the composition of which, in percentage weights, is given on Table V.

TABLE V

Ingredient	H_3
Dichlobenil	7.5%
Paraquat	5%
Dimethylsulfoxide	85%
Oxalic acid	2.5%

The diluted solution was applied in the same way as already described.

The results obtained are shown in Table VI.

Examination of these results shows that the combination of dimethylsulphoxide and oxalic acid has a very favourable effect on the destruction of weeds by the mixture of "Dichlobenil" and "Paraquat", used in weak doses.

Nearly all the weeds were destroyed, particularly, hardy plants such as toad-flax, bear's-bind, mallow, white clover and meadow speedwell.

Example 5.

On 8 October 1969, three solutions, H_4, H_5 and H_6, were spread on silicio-argillaceo-calcareous ground under the same general conditions as those described above.

The concentrations of weed-killers in the aqueous solutions used were generally higher than for the tests H_1, H_2 and H_3, but remain well below the doses normally used.

The composition of the concentrated formulae and the percentage dilution in the corresponding solutions for spraying are given in Table VII, as percentage weights.

TABLE VI

Type of Weed	Test H_3			
	9.10.69	10.10.69	14.10.69	8.11.96
Thistle	7	9	9	9
Goosefoot	7	9	9	9
Couchgrass	7	9	9	9
Wart-wort	7	9	9	9
Shiny crane's-bi	7	9	9	9
Greater plantain	5	7	9	9
Goosegrass	7	9	9	9
Corn sow-thistle	7	9	9	9
Toad-flax	0	1	5	8
Bear's -bind	2	5	8	8
Mallow	0	0	2	7
Black nightshade	7	9	9	9
Scarlet pimpernel	7	9	9	9
Chickweed	7	9	9	9
Meadow-grass	7	9	9	9
Dandelion	5	9	9	9
Spear-shaped plantain	7	9	9	9
Purslane	7	9	9	9
Ray-grass	7	9	9	9
Creeping buttercup	7	9	9	9
Knotgrass	1	1	7	9
Rumex (sorrel)	5	9	9	9
Common groundsel	7	9	9	9
White clover	7	9	9	9
Meadow speedwell	7	9	9	9

TABLE VII

Ingredient	H_4	H_5	H_6
Dichlobenil	15%	15 %	10%
Paraquat	5%	7.5%	5%
Dimethylsulphoxide	80%	77.5%	85%
Dilution	2%	2 %	3%

The results obtained are shown in Table VIII.

On 10 October 1969, a series of observations was also carried out, resulting in the allotting of reference numbers identical to those for the observations carried out on 9 October 1969, except as regards toad-flax and bear's-bind, the degree of destruction of which corresponded to number five for Test H_4, five for Test H_5 and six for Test H_6, and mallow, the destruction of which corresponded to number two for Test H_5 and six for Test H_6.

Analysis of the results obtained during these tests shows the highly effective herbicidal effect of compositions H_4, H_5 and H_6, although the quantity of "Dichlobenil" is five times less than in Test A, and that of "Paraquat" 3.6 times to 5 times less than in Test B.

This intensive herbicidal effect is shown particularly in the destruction of toad-flax, bear's-bind and mallow. The formula H_6, in 3% dilution, has a quite remarkable destructive effect on weeds. Not only were all the plants destroyed one month after treatment, but observation of the treated plot on 14 January 1970, namely more than three months later, showed that the soil remained perfectly free from weeds and that there were no new plantlets resulting from surface seeds.

TABLE VIII

Type of Weed	Test H_4			Test H_5			Test H_6		
	9/10 1969	14/10 1969	8/11 1969	9/10 1969	14/10 1969	8/11 1969	9/10 1969	14/10 1969	8/11 1969
Thistle	7	8	9	7	8	9	7	9	10
Goosefoot	7	8	9	7	8	9	7	9	10
Couchgrass	7	8	9	7	8	9	7	9	10
Wart-wort	7	8	9	7	8	9	7	9	10
Shiny crane's-bill	7	8	9	7	8	9	7	9	10
Greater plantain	7	8	9	7	8	9	7	9	10
Goosegrass	7	8	9	7	8	9	7	9	10
Corn sow-thistle	7	8	9	7	8	9	7	9	10
Toad-flax	2	6	8	2	6	8	5	8	10
Bear's-bind	2	6	8	2	6	8	5	8	10
Mallow	0	2	4	0	2	4	5	7	10
Black nightshade	7	8	9	7	8	9	7	9	10
Scarlet pimpernel	7	8	9	7	8	9	7	9	10
Chickweed	7	8	9	7	8	9	7	9	10
Meadow-grass	7	8	9	7	8	9	7	9	10
Dandelion	7	8	9	7	8	9	7	9	10
Spear-shaped plantain	7	8	9	7	8	9	7	9	10
Purslane	7	8	9	7	8	9	7	9	10
Ray-grass	7	8	9	7	8	9	7	9	10
Creeping buttercup	7	8	9	7	8	9	7	9	10
Knotgrass	7	8	9	7	8	9	7	9	10
Rumex (sorrel)	7	8	9	7	8	9	7	9	10
Common groundsel	7	8	9	7	8	9	7	9	10
White clover	7	8	9	7	8	9	7	9	10
Meadow speedwell	7	8	9	7	8	9	7	9	10

Example 6.

The two tests described in this example were carried out on 29 October 1969, on weeds growing in argillaceo-calcareous soil.

The solutions S_1 and S_2 were obtained by diluting the concentrated formulae H_6 mentioned in example 5, a 2% solution for S_1 and 3% for S_2.

A controlled test (Test C) was also carried out, using an aqueous solution of "Paraquat", identical to that used for Test B in example 1, as weed-killer solution.

Table IX shows the results obtained.

The results of Table IX show the great effectiveness of solutions obtained from synergic compositions according to the present invention, in particular for the total destruction of bear's-bind, madder-wort and meadow speedwell, on which solutions of only one weed-killer have no effect or only temporary effect.

TABLE IX

Type of Weed	Test C				Test S_1				Test S_2			
	31/10 1969	5/11 1969	21/11 1969	23/12 1969	31/10 1969	5/11 1969	21/11 1969	23/12 1969	31/10 1969	5/11 1969	21/11 1969	23/12 1969
Thistle	9	9	9	9	6	9	9	9	9	9	9	10
Chicory	9	9	9	9	6	9	9	9	9	9	9	10
Madder-wort	0	0	0	0	—(b)	—	—	—	5	5	9	10
Shiny crane's-bill	9	9	9	9	6	9	9	9	9	9	9	10
Greater Plantain	9	9	9	9	6	9	9	9	9	9	9	10
Goosegrass	9	9	9	9	6	9	9	9	9	9	9	10
Bear's-bind	0	0	0	0	2	6	6	8	5	8	9	10
Scarlet pimpernel	9	9	9	9	6	9	9	9	9	9	9	10
Spear-shaped plantain	9	9	9	9	6	9	9	9	9	9	9	10
Ray-grass	9	9	9	9	6	9	9	9	9	9	9	10
White clover	9	9	9	9	6	9	9	9	9	9	9	10
Meadow speedwell	9	9	9	0(a)	6	9	9	9	9	9	9	10

(a) Growth restarts
(b) No madder-wort in the plot treated during test S_1